Airborne Measurements of NO, NO_2, and NO_y

as Related to NASA's TRACE-A Field Program

Final Report (NAG-1-1415)
Period of Performance: 4/1/92 to 6/30/95

Submitted to:

National Aeronautics and Space Administration
Langley Research Center
Mail Stop 401 A
Hampton, Virginia 23665

Submitted by:

Dr. John Bradshaw, Principal Investigator
Dr. Scott Sandholm, Co-Investigator
School of Earth and Atmospheric Sciences
Georgia Institute of Technology
Atlanta, Georgia 30332-0340

Scientific Objectives

The Georgia Tech group's effort on NASA's GTE program and TRACE-A field mission primarily involved analysis and interpretation of the measurement data base obtained during the TRACE-A field campaign. These investigations focused on the distribution of ozone and ozone precursors over the south Atlantic and nearby continental regions of Africa and South America. The Transport and Atmospheric Chemistry near the Equator-Atlantic (TRACE-A) Mission was designed with the goal of investigating tropospheric trace gas distributions, sources, and photochemical state over the southern Atlantic.

Major scientific issues related to N_xO_y tropospheric chemistry addressed in this program included:

(1) What controls the tropospheric ozone budget over the southern Atlantic?

(2) What are the spatial distributions of CO, CO_2, NO, NO_2, NO_y, PAN, O_3, NMHC, H_2O_2, etc. over the southern Atlantic?

(3) How does long range transport of long-lived NO_y compounds affect the more reactive NO_x budget in the southern Atlantic troposphere?

NO_x concentrations play a pivotal role in controlling the photochemical O_3 lifetime in these environments. Transport of NO_x into the region in the form of longer lived N_xO_y compounds was examined in relation to comparing naturally occurring sources of NO_x (i.e., lightning and stratosphere/troposphere exchange) to those produced as a result of anthropogenic activity (e.g. biomass burning). Our measurements of NO_x/NO_y, in conjunction with other investigators' measurements of PAN and HNO_3, have been used for a detailed assessment of

total active nitrogen levels over the study regions, as well as the partioning of active nitrogen species in their various forms. This data base, in conjunction with other measurements (O_3, CO, H_2O NMHC's, etc.), was used to assess: (1) closure within the N_xO_y budget; (2) distribution of the more reactive NO_x and longer lived NO_y odd-nitrogen reservoir species within the troposphere; (3) the relative impact from long-range transport of odd-nitrogen reservoir NO_y components on the cycling of the more reactive odd-nitrogen species within the southern Atlantic; and (4) the relative photostationary state of the atmosphere relating to odd-nitrogen chemistry.

Our group's primary TRACE-A objective was the characterization of the factors controlling the distribution and fate of reactive nitrogen compounds over the equatorial and tropical South Atlantic and adjacent continental region. We particularly focused on determining the source of the large abundances of NO that were found to be ubiquitous within the free troposphere over this region and that contributed significantly to the levels of O_3 on a regional scale.

Summary of Results

The chemical characteristics of air masses over the tropical South Atlantic during September and October 1992 were analyzed in aged marine and continental outflow classifications. Comparison of the composition of aged Pacific air with aged marine air over the South Atlantic Basin from 0.3 - 12.5 km altitude indicated potential accumulation of long-

lived species during the local dry season. NO and NO_x were significantly enhanced (up to ~1 ppbv) above 10 km altitude and poorly correlated with the biomass burning tracers CO and CH_3Cl. In addition, median mixing ratios of NO and NO_x were essentially identical in aged marine and continental outflow air masses. The horizontal injection of biomass burning products over the South Atlantic, particularly water-soluble species and aerosol particles, were frequent below 6 km altitude. The deposition of atmospheric nitrogen and other nutrient species to oligotrophic tropical South Atlantic surface waters may have important implications for this marine ecosystem.

NO_x ($NO + NO_2$) mixing ratios in the 8 to 13 km region averaged 150 pptv and were greatly affected by what appeared as spatially large "plumes" (100 to 1,000 km) with NO enhancements of over 800 pptv. Other trace gases were also often enhanced within these plumes (e.g., C_2H_2, CO, CH_3Cl, CO_2, CH_4, C_3H_8, C_2H_6, and PAN). However, these tracers of surface emissions displayed inconsistent patterns of enhancement and attenuation with respect to one another and to NO. We analyzed these plumes for indications of coherent relationships between the enhanced levels of NO and the enhanced levels of biogenic and combustion related tracers. This analysis indicated that the tracer relationships were primarily produced by their common injection via deep convection into the upper troposphere. A corollary analysis using a combustion tracer reference frame in combination with meteorological analysis indicates that an efficient mechanism exists in the upper troposphere for recycling HNO_3 back into NO_x with a rate comparable to that predicted for HNO_3's formation. During the TRACE-A study period, this *in-situ* of NO_x was estimated to provide the equivalent of approximately 0.7 TgN/yr of NO_x

within this region's upper troposphere. This magnitude of local *in-situ* source is estimated to be equivalent to the combined inputs from lightning and biomass burning, which are both injected via deep convection. Our analysis also suggests that lightning can contribute as much as 50% of the external input of NO_x into this region of the upper troposphere with biomass burning possibly representing the remainder.

Publications (Co-Authored), Submitted for Publication

"Factors Influencing the Upper Free Tropospheric Distribution of Reactive Nitrogen Over the South Atlantic During the TRACE-A Experiment," S. Smyth, et al., Journal Geophys. Res. (submitted).

"Air Mass Characteristics Observed Over the Tropical South Atlantic, Africa, and Brazil During the Springtime," E.V. Browell, et al., Journal Geohys. Res. (submitted).

"Chemical Characteristics of Continental Outflow Over the Tropical South Atlantic Ocean from Brazil and Africa," R.W. Talbot, et al., Journal Geophys. Res. (submitted).

"The Origin of Ozone and NO_x in the Tropical Troposphere: A Photochemical Analysis of Aircraft Observations Over the South Atlantic Basin," D.J. Jacob, et al., Journal Geophys. Res. (submitted).

"Ozone, Hydroperoxides, Oxides of Nitrogen, and Hydrocarbon Budgets in the Marine Boundary Layer Over the South Atlantic," B. Heikes, et al., Journal Geophys. Res. (submitted).

"A comparison of aircraft and ground-based measurements of Mauna Loa Observatory, Hawaii during GTE PEM-WEST and MLOPEX II," E. Atlas, et al., Journal Geophys Res. (submitted).

"An Assessment of Western Pacific Photochemical Trends in Ozone As Inferred From PEM-WEST(A) Observations During Fall 1991," D.D. Davis, et al., Journal Geophys. Res. (submitted).

Undergraduate Student Researchers Associated with Project

Ms. Christy Robb

Ms. Nicole Shumaker

Mr. Vikram Reddy

Mr. Atul Kanvinde

Graduate Student Researchers Associated with Project

Mr. John Olson (Ph.D. candidate)

Mr. Rongpo Bai (Ph.D. candidate)

Mr. Walter Patterson

Post Doctoral Researcher Associated with Project

Dr. Scott Smyth